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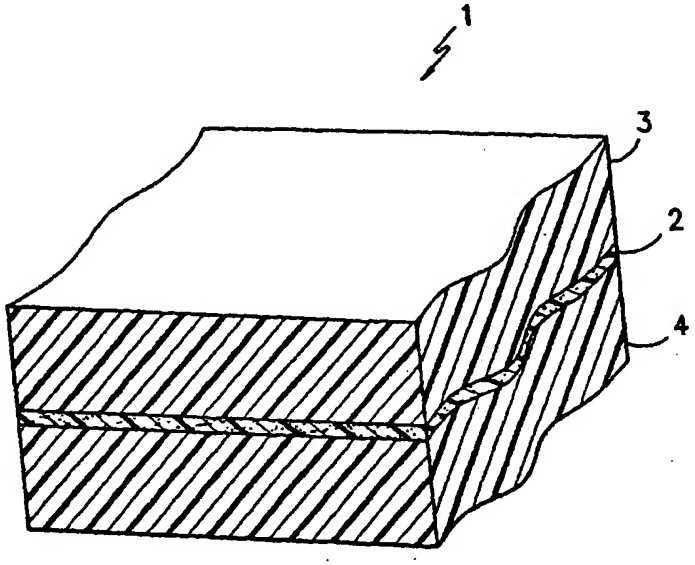
(54) Title: EVOH COPOLYMER HAVING COLORANT INCORPORATED THEREIN



(57) Abstract: A multi-ply sheet (1) is provided having first (3) and second (4) thermoplastic films layered on either side of an EVOH resin barrier film (2), and a poly(oxyalkylene) substituted colorant is incorporated in the EVOH resin to provide coloration and improve the barrier properties of the resin.

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EVOH COPOLYMER HAVING COLORANT INCORPORATED THEREIN

This invention relates to a colored EVOH copolymer barrier film and, in particular, to a multi-layered container made from such a film.

Background of the Invention:

Beverage containers made from thermoplastic polymer resins have been developed to replace glass. Plastic containers have many advantages including being lightweight, relatively inexpensive and recyclable. The performance requirements of any beverage container are that it possess barrier properties both for the liquid contained therein, and for gases, such as carbon dioxide, which may escape from the container, and oxygen, which may enter the container and react with the contents. Examples of plastic containers may be found in the following United States patents: 5,061,534; 5,069,955; 5,154,789; 5,281,360; 5,346,735; 5,705,111; and 5,866,649.

Improving the barrier properties of the films used in plastic containers is the subject of ongoing research and development. Kim et al. U.S. Patent No. 5,314,987 discloses a polyester / nylon blends having improved barrier properties. Chuu et al. U.S. Patent No. 5,605,996 discloses polymer compositions comprising oxygen scavenging compounds having unsaturated carbon to carbon bonds. A barrier film composition incorporating cyclodextrins is disclosed in Wood et al. U.S. Patent No. 5,882,565.

Another important consideration in the use of plastic containers is their recyclability. If multiple layer films are employed, that is, layers made from more

than one kind of polymer, it will generally be necessary to separate the polymers as part of the recycling process. Peters et al. U.S. Patent No. 5,840,772 discloses a method of separating multilayered plastic structures.

The plastic containers may be colored; for example amber colored containers for beer and green colored containers for soft drinks. In the case of multi-layered structures, it may be desirable to color only one layer. Thomas U.S. Patent No. 4,919,855 discloses adding an UV fluorescent compound to a layer of the laminate. After the laminate is made into a container, one may illuminate the container with a suitable light source and verify that the layer containing the fluorescent compound has been uniformly distributed. Okudaira et al. U.S. Patent No. 4,535,901 discloses a multi-ply blow molded vessel. A colorant, preferably in a concentration of not more than 0.5 parts by weight per 100 parts by weight of the plastic resin, may be incorporated into the middle layer of the vessel.

In order to obtain deep shades of color, comparable to glass containers, it is necessary to add relatively high concentrations of colorant to the plastic. If one desires to restrict the use of colorant to only one layer of a multi-layer film, the concentration of the colorant in that layer must be significantly increased, if the desired shade is to be maintained. As the concentration of the colorant is increased, however, the properties of the polymer resin can be adversely affected. For example, high concentrations of dyes or pigments can diminish the barrier properties of a film. Additionally, the dye or pigment can have a detrimental effect on the viscosity of the polymer resin during melt compounding and extruding,

especially when one is forming a laminate made of two or more different kinds of resin.

Poly(oxyalkylene) substituted colorants have been disclosed for use in coloring thermoplastic resins in Baumgartner et al. U.S. Patent Nos. 4,640,690 and 4,842,141. The primary application of the technology has been in polyolefin resins. At relatively high colorant loading levels, however, the poly(oxyalkylene) substituted colorants can significantly lower the viscosity of the polyolefin resin melt (i.e. increase the melt flow rate), which in turn affects the conditions under which the resin can be extruded. Additional references disclosing the use of poly(oxyalkylene) substituted colorants in thermoplastic resin include Kluger et al. U.S. Patent No. 4,978,362; Kluger et al. U.S. Patent No. 5,177,200; and Danielson et al. U.S. Patent No. 5,240,980.

Summary of the Invention:

Therefore, an object of the invention is to provide a colorant for an EVOH copolymer film, which does not have a detrimental effect on the film's barrier properties. Another object of the invention is to provide a colorant, which does not significantly lower the melt viscosity of the EVOH copolymer film. Yet another object of the invention is to provide a colored EVOH copolymer resin which may be coextruded with other thermoplastic resins to form a laminate. Further objects of the invention include providing a laminate in which only the EVOH copolymer film is colored; a laminate having an EVOH copolymer film sandwiched between inner and outer thermoplastic resin films; and a bottle formed by blow molding the novel laminate.

Accordingly, an EVOH copolymer resin film is provided having a poly(oxyalkylene) substituted colorant incorporated throughout. In one embodiment of the invention, the colored EVOH resin film is layered between inner and outer films of thermoplastic resin and formed into a bottle by blow molding.

The present invention, in its various embodiments, has the following advantages and features:

- The EVOH copolymer resin film layer can be shaded deeply and the other layers of the multi-ply sheet allowed to remain clear, thereby increasing the amount of uncolored resin recovered from recycling articles made from the sheet.
- The poly(oxyalkylene) substituted colorant has the unexpected and valuable effect of improving the barrier properties of the EVOH resin, when the colorant is incorporated in the resin.
- The melt viscosity of the colored EVOH resin remains sufficiently high to allow coextrusion with other layers of thermoplastic resin to form a multi-ply sheet.

Brief Description of the Drawings

Figure 1 is a perspective of a multi-ply sheet having a colored EVOH resin film sandwiched between clear thermoplastic films.

Detailed Description of the Invention

Without limiting the scope of the invention, the preferred embodiments and features are hereinafter set forth.

Unless otherwise indicated, all parts and percentages are by weight and conditions are ambient, i.e. one atmosphere of pressure and 25°C.

Average molecular weights are based on the number average molecular weight (M_n).

All United States patents, which are cited in the specification, are hereby incorporated by reference.

The ethylene-vinyl alcohol (EVOH resin) copolymer employed in the present invention can be characterized as the family of copolymers made by hydrolyzing ethylene-vinyl acetate copolymers with high vinyl acetate content. Copolymers containing from about 20 to 45 mole % ethylene are preferred, and are especially useful as barriers to many vapors and gases.

The EVOH resin may contain minor amounts (less than 50 wt.%) of other polymers added to improve the processability and other properties of the resin, such as nylon, polyetheramide block copolymer, polyolefin, and poly(vinyl alcohol). The EVOH resin composition may include conventional polymer additives, for example, plasticizers, antioxidants, stabilizers, lubricants, flame retardants, nucleating agents, UV absorbers, and other additives known to those skilled in the art.

The poly(oxyalkylene) substituted colorant of the present invention is characterized by an organic chromophore having at least one poly(oxyalkylene) substituent. A wide variety of organic chromophores are suitable for use in the present invention. Examples of useful chromophores include: nitroso, nitro, azo and polyazo, diarylmethane, triarylmethane, xanthene, acridine, quinoline,

methine, thiazole, indamine, indophenol, lactone, aminoketone, hydroxyketone, stilvene, azine, oxazine, thiazine, anthraquinone, phthalocyanine and indigoid chromophore groups. Of particular interest are azo, methine, triarylmethane, anthraquinone and phthalocyanine chromophore groups.

One or more poly(oxyalkylene) substituents are bonded to the organic chromophore. The poly(oxyalkylene) substituent may be characterized as a straight or branched chain, which is the reaction product of from 3 to 100 C_2-C_4 alkylene oxide monomer units. In a preferred embodiment, the poly(oxyalkylene) substituents are primarily comprised of the reaction product of from 5 to 50, most preferably 8 to 40 monomer units selected from ethylene oxide, propylene oxide or random and block copolymers thereof. Minor amounts of glycidol, butylene oxide and other compatible monomers may also be incorporated into the substituent. For example, glycidol monomers may be incorporated into the poly(oxyalkylene) substituent to promote branching. When enhanced branching is desired, preferably from 2 to 10 glycidol units are provided per poly(oxyalkylene) chain.

The chromogen may be covalently bonded to the poly(oxyalkylene) substituent by a linking group selected from N, NR, O, S, S_2, SO_2N, SO_2NR, CO_2, CON or CONR, where R is H, C_1-C_{12} alkyl, phenyl or benzyl. Preferably, the linking group is N, NR, O, SO_2N or SO_2NR. Two poly(oxyalkylene) substituents may be bonded to the chromophore through a trivalent linking group. The number of poly(oxyalkylene) chains per chromophore may be from 1 to 6, preferably 1 to 4, most preferably 1, 2 or 3.

The precise identity of the terminal group of the poly(oxyalkylene) substituent is not believed to be critical, insofar as the functioning of the colorant is concerned, but may have an affect on solubility. By way of example, the end group may be selected from –SH, -OH, $-NH_2$, or may be ester capped, such as by reaction with stearic acid, or dodecyl succinic acid or anhydride. Preferably, the poly(oxyalkylene) substituent has a hydroxyl terminal group.

Synthesis of organic chromophores containing poly(oxyalkylene) substituents are disclosed in Kuhn US 3,157,633, Brendle US 4,167,510, Cross et al. US 4,284,729, Baumgartner et al. US 4,732,570, Moody et al. US 5,290,921 and Zhao et al. US 5,948,152.

In addition to poly(oxyalkylene) substituted colorants having substantial absorbance and emission in the visible electromagnetic spectrum, the term poly(oxyalkylene) substituted colorants is also intended to include those organic chromophores which exhibit fluorescence. Examples of fluorescent poly(oxyalkylene) substituted chromophores may be found in Kluger et al. U.S. Patent No. 4,992,204.

The colorant may be incorporated into the EVOH resin using conventional techniques such as those employed to incorporate other additives. For example, the colorant may be incorporated into the resin by simply adding it to the resin while the resin is in a plasticized or molten state. One such method is to melt compound the colorant in the EVOH resin by injecting the colorant into the molten polymer in a screw compounder. Alternatively, the colorant may be preblended with the EVOH resin, and then, introduced into the melt compounding equipment.

Concentrates of the colorant and EVOH resin may be formed, which can then be melt compounded with uncolored EVOH resin, to provide lighter or blended shades. Those skilled in the art will recognize that virtually any combination of poly(oxyalkylene) substituted colorants can be made to provide the desired color of resin. The poly(oxyalkylene) substituted colorants of the present invention may be provided in liquid form. Thus, they may be added to the thermoplastic polymer melt in solvent-free form, rather than in the form of solutions or dispersions. Alternatively, the poly(oxyalkylene) substituted colorant may be dispersed in a suitable solvent or dispersing medium prior to being incorporated into the EVOH resin.

In cases where the colorant is incorporated into the EVOH resin by melt compounding, the composition may be extruded, as is well known to those skilled in the art. For example, the composition may be extruded in the form of a sheet or made into pellets. The extrudate may be further processed by, calendering, compression molding or other process. Alternatively, the colorant and EVOH resin composition may be cast. If a solvent is present, it can be evaporated at this stage.

The poly(oxyalkylene) substituted colorant can be incorporated into the EVOH resin at levels of from 0.01 to 25 wt.%, preferably 0.5 to 15 wt.%, most preferably 1 to 10 wt.%, based on the weight of the composition.

Conventionally, a web of plastic that is 10 mils (0.25 mm) or less in thickness is referred to as a film, and webs having a thickness of greater than

10 mils (0.25 mm) is referred to as a sheet. The definitions are generally adhered to herein, however, there is no intention to provide a bright line distinction between films and sheets. The term "film" is used herein to describe a single layer of plastic web, and the term "sheet" is used to describe a multi-ply article of two or more films.

The colored EVOH resin composition may be formed into a film of virtually any thickness. By way of example, the composition may be formed into films having a thickness ranging from 0.5 to 25 mils, preferably 1 to 12 mils. Since the colored EVOH resin will typically be a more expensive component than other thermoplastic resins used in a multi-ply sheet, films less than 10 mils are typically employed.

The melt viscosity of the colored EVOH resin is an important factor in its processability. The melt viscosities reported herein are measured by conventional melt flow rate methods, according to ASTM D1238. Measurements reported herein were taken on a Ray-Ran Melt Flow Indexer Model MK-1. Colored EVOH resin compositions having a melt flow rate ranging from 0.7 to 20 grams/10 minutes are particularly useful for forming films by extrusion and forming laminates by coextrusion. Preferably, the melt flow rate ranges from 1 to 5 grams/10 minutes.

Example 1:

A blend of poly(oxyalkylene) substituted colorants, to make an amber shade, was formulated for subsequent testing. The composition comprised 15.8% yellow colorant, 18.1% red colorant, 16.5% orange colorant, 14.0% cyan colorant,

25.6% UV absorber, 5.0% Span 80™, a nonionic surfactant available from ICI, and 5.0% Tween 40™, a nonionic surfactant available from ICI. The yellow component of the amber blend was a methine colorant, as described by Baumgartner et al in US patent 4,640,690, except that the resulting chromophore is the product of condensing p-formyl aniline, having 16 moles of ethylene oxide plus 10 moles of propylene oxide, with ethylcyanoacetate. The red component is an azo colorant, as described by Baumgartner et al in US patent 4,640,690 in Example 1, except that the amine used is 2-amino-4-methyl benzothiazole, which is coupled with meta-toluidine, having a block polymer of 16 moles of ethylene oxide and 10 moles of propylene oxide per mole of meta-toluidine. The orange component of the amber mixture is a bis azo colorant, described by Stephens et al in US patent 5,864,002 in Example 2, except that the poly(oxyalkylene) component is the product of reacting 16 moles of ethylene oxide and 10 moles of propylene oxide per mole of meta-toluidine. The blue component is described by Zhao et al in US Patent 5,948,152 in Example 1.

A polymeric methine ultarviolet light absorber was prepared as follows: one thousand parts of p-formyl-N,N-polyoxyethyleneaniline (27 moles EO) were mixed with one hundred twenty four parts of diethyl malonate and thirty part of ammonium carbonate. The mixture was heated between 70 and 75 °C for 10 hours. The reaction was monitored by the UV-Vis spectra of the mixture. When the reaction was completed as indicated by the Uv-Vis spectra, the product was further stripped under reduced pressure to give the final product.

These colorants and other additives were then blended together to obtain the desired shade of amber. It was then melt compounded into three types of thermoplastic resins. These included a polypropylene random copolymer, Fina 7620Z 12 melt flow rate; a low density polyethylene, Quantum Chemical NA 860008 24.5 melt flow rate; and an ethylene vinyl alcohol copolymer resin, Evalca EP-F104-AW 4 melt flow rate. The ethylene vinyl alcohol copolymer (EVOH) was dried according to the manufacturer's instructions prior to its compounding. The amber blend of polymeric colorant was melt compounded on an American Leistritz 34 millimeter diameter counter-rotating twin screw compounder, outfitted with a Zenith gear pump for injection of the liquid colorant into the molten polymer. In each case, the liquid colorant was loaded at 2.5%, 5.0%, and 10.0% by weight of the thermoplastic polymer. The blended melt was extruded into a strand, water cooled, and pelletized.

In all cases, virgin thermoplastic resin was also extruded under the same conditions in order to give a control with the same thermal history as the samples with colorant incorporated.

The pellets of compounded blends were then tested for their melt viscosity by conventional melt flow rate measurements, according to ASTM D1238 on a Ray-Ran melt flow indexer model MK-1. The temperature used for each polymer was its standard temperature, (230°C for polypropylene and 190°C for the low density polyethylene and ethylene vinyl alcohol) as was the weight used with the device (2160 grams).

Table 1

Color loading	Polypropylene		Low density polyethylene		Ethylene vinyl alcohol	
	Melt flow rate	% increase over control	Melt flow rate	% increase over control	Melt flow rate	% increase over control
Control	11.2	0	28.1	0	2.5	0
2.5%	16.1	44	32.0	14	2.6	4
5.0%	18.1	62	64.8	131	3.4	36
10.0%	50.2	348	78.8	180	4.1	64

The pellets of compounded ethylene vinyl alcohol copolymer and colorant blends were compression molded on a Carver Laboratory Press, Model 2697, compression molder in a sheet mold to give a film of from 7 to 8 mils in thickness. In all cases, the color uniformity of the films with polymeric colorants was very good, with no streaks or specks of color visually evident. The film was then tested for its oxygen transmission rate on a Mocon 2-20 H module, and according to ASTM D-3985. The test conditions were 23°C and 0% relative humidity.

Table 2

Color loading (EVOH)	O_2 transmission rate (cc/100 in^2/24 hours)
Control	0.0876
2.5%	0.0440
10.0%	0.0312

Example 2:

A yellow methine, poly(oxyalkylene) substituted colorant having an ester cap on the substituent group was melt compounded into EVOH resin, Evalca EP-F104-AW (nominal melt flow rate of 4 g/10 min). The yellow colorant was synthesized according to Example 1 herein, except that (i) m-toluidine having 2 moles of ethylene oxide/14 moles of propylene oxide/8 moles of ethylene oxide

was used in the condensation; and (ii) the resulting colorant was then allowed to react with dodecylsuccinic anhydride according to Example 1 of U.S. 5,176,745, to provide an ester cap. The colorant was added at loadings of 2.5 wt% and 5 wt% into the ethylene vinyl alcohol by melt compounding as described in Example 1.

The melt flow rate was measured on a Ray-Ran melt flow indexer, as described in Example 1 herein.

The melt flow rate results are shown in Table 3.

Table 3

Melt flow index of poly(oxyalkylene) substituted colorant in EVOH resin

Description	Colorant Loading in EVOH (wt%)	Average Melt Flow Index
Virgin EVOH Resin	N/A	4.5 g/10 min
Capped Yellow	2.5%	5.6 g/10 min
Capped Yellow	5.0%	4.5 g/10 min

Example 3:

For a comparative example, various dyes were compounded into EVOH resin, and evaluated for their dispersion and oxygen permeation rates. Disperse and reactive dyes were chosen and evaluated by melt compounding them into Evalca EP-F104AW at 0.5%. The loadings of the dyes being evaluated are lower than that of the poly(oxyalkylene) substituted colorant examples due to the dye's greater tinctorial strength. To demonstrate the relative strength of the color in the samples, the % reflectance was measured at the wavelength of maximum light absorption. Lower reflectance values indicate a higher strength of color. This measurement was done on a Datacolor International CS-5 spectrophotometer. The dyes are

compounded into the polymer by way of a 1 inch single screw (32:1 length:diameter ratio) Killion extruder with a melt temperature of 385°F. The resulting pellets are then compression molded into films of from 7 to 8 mils in thickness, as described in Example 1 above. The films are then tested for oxygen permeation as described in example 1. The results of the dispersion and oxygen permeation follow:

Table 4

	Oxygen transmission rate (cc/100 in^2/24 hours)	Dispersion	% Reflectance @ Lambda Max.
Control; Evalca EP-F104AW EVOH	0.087	N/A	N/A
Disperse yellow KHM @ 0.5%	0.120	Poor	9.57
Disperse Blue GLF @ 0.5%	0.126	Good	6.59
Disperse Red KFFN @ 0.5%	0.108	Good	4.29
Reactive Red 3BS @ 0.5%	0.108	Poor	37.00
Reactive Yellow RNL @ 0.5%	0.108	Very poor	11.30
Reactive Blue RGB @ 0.5%	Greater than 600	Very poor	15.68
Inventive amber of example 1 @ 2.5%	0.0440	Excellent	N/A
Inventive amber of example 1 @ 10%	0.0312	Excellent	N/A

In addition to providing a barrier to the transmission of O_2, films made from the colored EVOH resin of the present invention are also useful as barriers to carbon dioxide and nitrogen. Colored EVOH resins having an oxygen permeability of less than 0.1 cc/100 in^2/24 hours for a 7 mil thick film at 0% relative humidity, are especially useful in beverage containers made from multi-ply sheets. Preferably, the colored EVOH resins have an oxygen permeability of less than 0.05 cc/100 in^2/24 hours for a 7 mil thick film at 0% relative humidity. Quite unexpectedly, incorporation of the poly(oxyalkylene) substituted colorant into the EVOH resin has been found to reduce the oxygen transmission rate by approximately one-half at a loading of 2.5 wt.%, and by approximately 65% at a colorant loading of 10 wt.%.

In a preferred embodiment of the invention, the colored EVOH resin is a component of a multi-ply sheet. For example, the colored EVOH resin may be sandwiched between first and second layers, sometimes referred to as inner and outer layers in contemplation of the multi-ply sheet being formed into a container. Those skilled in the art will recognize that any number of additional layers may be included in the sheets, and sheets having five layers or more are known. The films which make up the multi-ply sheet may be bonded together with adhesive coatings or other type of tie layer, but in most cases, such adhesives are not necessary. If desirable, additional layers of reinforcing materials such as textile scrims and paper coatings may be applied.

The multi-ply sheet may be formed by any of a number of methods known to those skilled in the art, including coextrusion, lamination, coating, extrusion coating and pressure, with or without heat applied. Preferably, the multi-ply sheet is formed by coextruding the colored EVOH resin film between at least two other thermoplastic films. The sheet may be made into any practical thickness. For use in beverage containers, such as beer bottles, typically have a wall thickness of 5 to 25 mils, preferably 10 to 20 mils.

Any number of thermoplastic resins may be used to form the multi-ply sheet in addition to the colored EVOH resin. By way of example, suitable thermoplastic resins include polyester, polyamide, polyolefin, polycarbonate, polystyrene, polyacrylic, poly(vinyl chloride), poly(vinylidene chloride), acrylonitrile and cellulosic resin. In a preferred embodiment, the thermoplastic resin is polyester or polypropylene. Blends of thermoplastic polymers may be

used as well. The thermoplastic resin, other than the EVOH resin, is preferably colorless, which is intended to mean resins having an absorbance of less than 0.1 in the visible spectrum.

An example of a multi-ply sheet according to the present invention is shown in Figure 1. Multi-ply sheet 1 is constructed of a colored EVOH film 2 having a thickness of approximately 1 mil, which is sandwiched between clear thermoplastic resin layers 3 and 4, having a thickness of approximately 7 mils each.

The colored EVOH film, and especially the multi-ply sheets of the present invention has wide application in the field of packaging and protective films. In particular, the multi-ply sheet may be formed into a bottle for packaging beverages. Techniques for forming a multi-ply sheet into a beverage container are known to those skilled in the art and are disclosed in many of the references cited herein. For example, beverage containers may be formed by injection molding, extrusion blow molding and stretch blow molding. Beverage containers which are colored brown or green have been found to be particularly useful in protecting the beverage contained therein. Many beverages, such as beer, are very sensitive to oxygen and a typical performance requirement is that less than one part per million of oxygen be transmitted to the beer over a six month period, at ambient conditions (50% relative humidity).

There are, of course, many alternative embodiments and modifications of the invention, which are intended to be included in the scope of the following claims.

What I claim is:

1. A composition comprising an EVOH copolymer resin and a poly(oxyalkylene) substituted colorant, incorporated throughout the resin, in a concentration of from 0.01 to 25 weight %, based on the weight of the composition.
2. The composition of Claim 1 wherein the colorant is selected from the group consisting of nitroso, nitro, azo and polyazo, diarylmethane, triarylmethane, xanthene, acridine, quinoline, methine, thiazole, indamine, indophenol, lactone, aminoketone, hydroxyketone, stilvene, azine, oxazine, thiazine, anthraquinone, phthalocyanine and indigoid chromophore groups and has from one to six poly(oxyalkylene) substituents, each substituent is comprised of the reaction product of from 3 to 100 monomer units selected from the group consisting of ethylene oxide and propylene oxide.
3. The composition of Claim 1 wherein the composition is comprised of from 0.5 to 15 weight % of the colorant.
4. The composition of Claim 1 wherein the colorant is selected from the group consisting of azo, methine and phthalocyanine chromophores, and has from one to six poly(oxyalkylene) substituents, each substituent is comprised of the reaction product of from 5 to 50 monomer units selected from the group consisting of ethylene oxide and propylene oxide.
5. The composition of Claim 1 wherein the composition is comprised of from 1 to 10 weight % of the composition.
6. The composition of Claim 1 having a melt flow rate in the range of from 1 to 12.

7. The composition of Claim 1 having an oxygen permeability of less than 0.1 cc/100 in^2/24 hours for a 7 mil thick film at 0% relative humidity.

8. The composition of Claim 1 having a melt flow rate in the range of from 1.5 to 7.5 and an oxygen permeability of less than 0.05 cc/100 in^2/24 hours for a 7 mil thick film at 0% relative humidity.

9. An article comprising an EVOH copolymer resin film having a thickness of from 0.1 to 15 mils, wherein a poly(oxyalkylene) substituted colorant is incorporated throughout the resin, in a concentration of from 0.01 to 25 weight %, based on the weight of the film.

10. The article of Claim 9 wherein the colorant is selected from the group consisting of nitroso, nitro, azo and polyazo, diarylmethane, triarylmethane, xanthene, acridine, quinoline, methine, thiazole, indamine, indophenol, lactone, aminoketone, hydroxyketone, stilvene, azine, oxazine, thiazine, anthraquinone, phthalocyanine and indigoid chromophore groups and has from one to six poly(oxyalkylene) substituents, each substituent is comprised of the reaction product of from 3 to 100 monomer units selected from the group consisting of ethylene oxide and propylene oxide.

11. The article of Claim 9 wherein the film is comprised of from 0.5 to 15 weight % of the colorant.

12. The article of Claim 10 wherein the colorant is selected from the group consisting of azo, methine and phthalocyanine chromophores, and has from one to six poly(oxyalkylene) substituents, each substituent is comprised of the

reaction product of from 5 to 50 monomer units selected from the group consisting of ethylene oxide and propylene oxide.

13. The article of Claim 9 having a melt flow rate in the range of from 1.5 to 7.5 and an oxygen permeability of less than 0.1 cc/100 in^2/24 hours for a 7 mil thick film at 0% relative humidity.

14. The article of Claim 9, further comprising first and second thermoplastic resin films layered on either side of the EVOH copolymer film, to form a sheet having at least three plies.

15. The article of Claim 14, wherein the first and second films do not contain EVOH copolymer.

16. The article of Claim 14 wherein the first and second films are comprised of thermoplastic resin selected from the group consisting of polyester, polyamide, polyolefin, polycarbonate, polystyrene, polyacrylic, poly(vinyl chloride), poly(vinylidene chloride), acrylonitrile, cellulosic resin and blends thereof.

17. The article of Claim 15 wherein the first and second films are colorless.

18. The article of Claim 17 wherein the article is in the shape of a bottle.

19. The article of Claim 17 wherein the bottle is the product of the process of extrusion or stretch blow molding.

20. The article of Claim 17 wherein the colorant comprises from 0.5 to 15 weight % of the EVOH film and is selected from the group consisting of azo, methine and phthalocyanine chromophores, and has from one to six poly(oxyalkylene) substituents, each substituent is comprised of the reaction product of from 5 to

50 monomer units selected from the group consisting of ethylene oxide and propylene oxide.

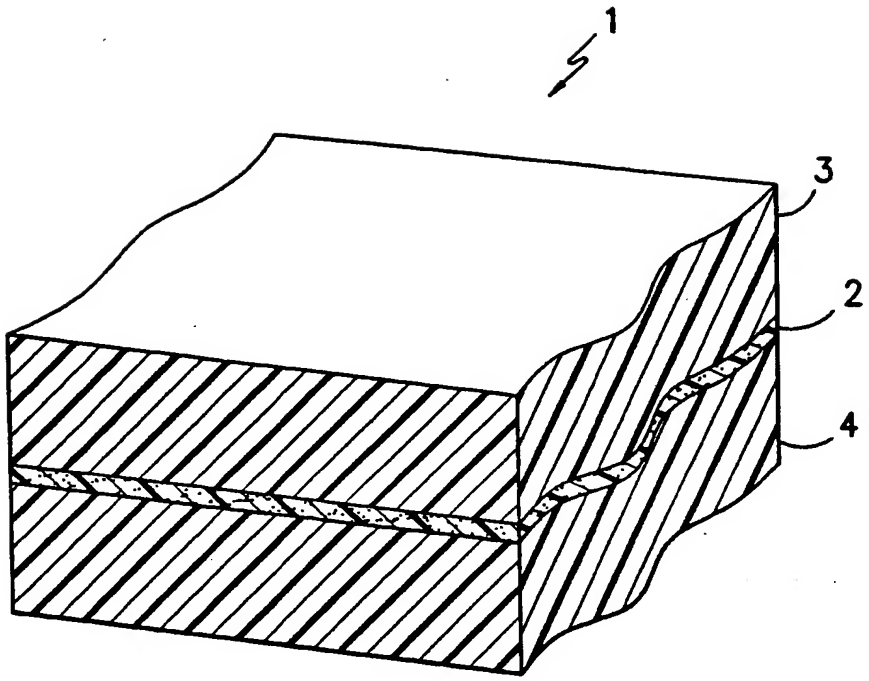

FIG. –1–

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/28089

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :B65D 23/00; B32B 27/00
US CL : 428/35.7, 36.7
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/35.7,36.7; 215/12.1,12.2; 8/506; 524/81,88,190,512-514,583,585

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,535,901 [OKUDAIRA et al] 20 August 1985, col. 3, lines 55-68, col. 4, lines 27-34, col. 5, lines 57-68, col.6, lines 7-23, col.8, lines 11-21, col. 10, lines 46-55.	1-20
Y	US 4,732,570 [BAUMGARTNER et al] 22 March 1988, col. 2, lines 30-68, col. 3, lines 49-68, col. 4, lines 1-23, col. 5, lines 1-9.	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 DECEMBER 2000	16 JAN 2001
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer PRENA DYE Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)★

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/28089

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

EAST 1.1
Search terms: ethylene vinyl alcohol, alkylenyloxy-substituted, pigment, dye, chromophore, ethylene oxide, propylene oxide, barrier, multilaminate, multilayer, bottle